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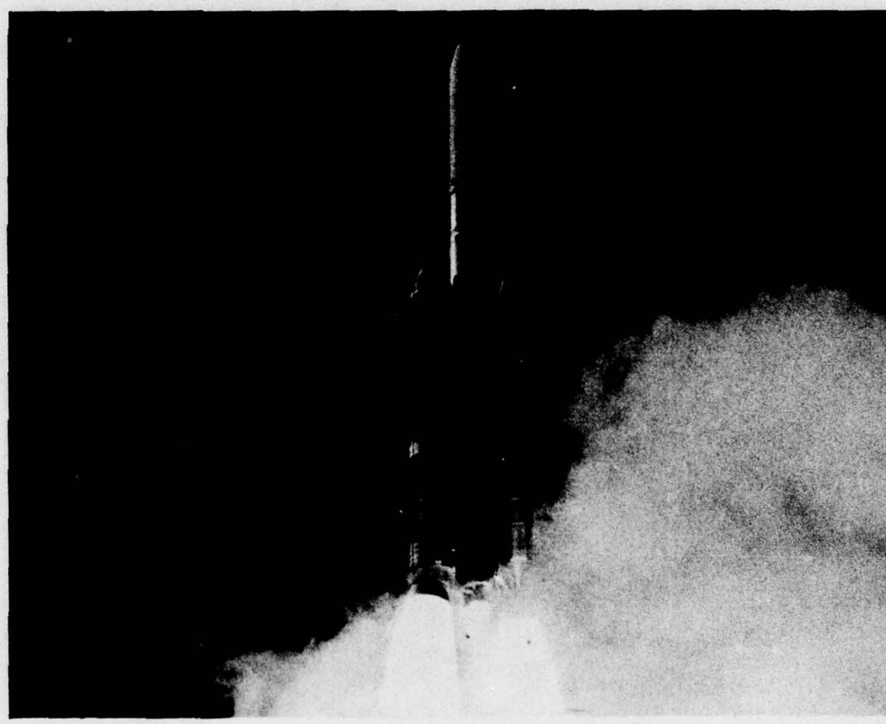

7—11 March 1977

Antelope Valley Inn

Lancaster, California

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ROCKET COMBUSTION
COMBUSTION DIAGNOSITCS

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

This report contains abstracts from the 1977 Joint AFOSR/AFRPL Rocket Propulsion Research Meeting held 7-11 March 1977 at the Antelope Valley Inn, Lancaster, CA. Presentations include research work sponsored by the two organizations as well as the work conducted in-house. Army and Navy combustion overviews are also contained as well as a Window-on-Science presentation from ONERA.

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6 AGENDA

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ROCKET PROPULSION RESEARCH MEETING (1977)
Antelope Valley Inn
Lancaster, ~~CA~~ California
7-11 March 1977.

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Bernard T. Wolfson

11 Mar 77

12 57p.

Monday*
7 Mar 77

0900	-	REGISTRATION
0930	-	ANNOUNCEMENTS: B. Wolfson; AFOSR
0945	-	WELCOME: R. Weiss; AFRPL
1000	-	AFRPL ACTIVITIES ASSOCIATED WITH DEVELOPMENT OF ELECTRIC SPACE THRUSTERS - TECHNOLOGY NEEDS AND RESEARCH REQUIREMENTS: G. Engelbreit and S. Pruitt; AFRPL
1030	-	COFFEE BREAK
1100	-	PARTICLE INTERACTIONS IN COLLOID EXHAUST PLUMES AND EFFECTS OF A DISTRIBUTION OF DROPLET SIZES: J. Perel and J. Mahoney; Phrasor Technology
1130	-	PLASMA ACCELERATION IN PULSED ABLATIVE ARC DISCHARGES: D. Palumbo and M. Begun; Fairchild Republic Company
1200	-	LUNCH
1330	-	MECHANISMS OF MAGNETOPLASMADYNAMIC ARC JET ACCELERATION PROCESSES: G. Cann and A. Ducati; Technion, Inc
1400	-	PULSED PLASMA ACCELERATION IN STRONG BIAS MAGNETIC FIELDS FOR ELECTRIC PROPULSION APPLICATION: C. L. Dailey; TRW Systems
1430	-	EXECUTIVE SESSION FOR AFOSR CONTRACTORS/GRANTEES: B. T. Wolfson; AFOSR
1500	-	ADJOURN

*Sessions will be held in Parlor 1, Monday, 7 March and Tuesday, 8 March. Erosive Burning/Velocity Coupling will be held in Parlor 2 at the same time.

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Tuesday*
8 Mar 77

0800	-	REGISTRATION
0830	-	KINETICS OF METAL OXIDE FORMATION: D. Mann; AFRPL
0900	-	PARTICLE OPTICAL PROPERTIES MEASUREMENTS (POPM) PROGRAM: J. Dowling and C. Randall; Aerospace Corporation
0930	-	SHOCK TUBE MEASUREMENTS OF MOLECULAR BAND STRENGTHS ASSOCIATED WITH BORON PROPELLANTS: A. Russo and D. Boyer; Calspan Corporation
1000	-	COFFEE BREAK
1030	-	LASER FLUORESCENCE MEASUREMENTS OF VIBRATIONAL ENERGY TRANSFER IN WATER AND AMMONIA: F. E. Hovis, J. Finzi and C. Bradley Moore; University of California
1100	-	KINETIC REACTION COEFFICIENTS IN ROCKET EXHAUST PLUMES: W. Snow, L. Schearer, K. Nygaard and R. Corbin; University of Missouri
1130	-	TRANSLATIONAL EXCITATION OF CO_2 TO A RADIATING STATE: Subbarao Ryali and J. B. Fenn, Yale University; C. E. Kolb; Aerodyne Research, Inc
1200	-	LUNCH
1330	-	ANALYTICAL INVESTIGATION OF MULTINOZZLE PLUME FLOW FIELDS: S. Rudman; Grumman Aerospace Corporation
1400	-	PHYSICAL/CHEMICAL PROCESSES CONTROLLING LOW ALTITUDE ROCKET EXHAUST PLUME VISIBILITY: Roger D. Thorpe; AeroChem Research Labs., Inc
1430	-	BREAK
1500	-	NONEQUILIBRIUM PROPERTIES OF EXHAUST PLUMES: M. Branch; University of Colorado
1530	-	UNSTEADY PLUME MODELING FOR HIGH ACCELERATION ROCKET LAUNCH: John I. Erdos; General Applied Science Labs., Inc
1600	-	CONDENSATION AND PARTICLES IN EXHAUST PLUMES: J. W. L. Lewis and W. D. Williams; ARO, Inc
1630	-	CREATION AND DESTRUCTION OF VIBRATIONALLY EXCITED OH: Glenn C. Light; Ivan A. Getting Labs., The Aerospace Corp
1700	-	ADJOURN

Wednesday
9 Mar 77

0800	-	REGISTRATION
0830	-	ANNOUNCEMENTS: T. Meier; AFOSR
0845	-	WELCOME: R. Weiss; AFRPL
0900	-	THE AFRPL BASIC RESEARCH PROGRAM: L. Quinn; AFRPL
0930	-	ARMY COMBUSTION RESEARCH: Carl W. Nelson; U. S. Army Ballistic Research Laboratory
1000	-	COFFEE BREAK
1030	-	NAVY RESEARCH IN SOLID PROPELLANT COMBUSTION: R. Derr; NWC China Lake
1100	-	UNSTEADY PROCESSES IN SOLID PROPELLANT COMBUSTION: A. Crespo and M. Kindelan; INTA
1130*	-	LUNCH
1330	-	RECENT RESEARCH AT ONERA ON COMBUSTION INSTABILITY AND EROSIVE BURNING: P. Kuentzmann and G. Lengelle; ONERA
1430	-	ROTATING VALVE FOR VELOCITY COUPLED COMBUSTION RESPONSE STUDIES: R. S. Brown, P. G. Willoughby, and V. L. Kelly; Chemical Systems Division, United Technologies
1500	-	RESEARCH ON UNSTEADY COMBUSTION PROCESSES: L. Caveny, M. Micci, A. Gany and M. Summerfield; Princeton University
1530	-	COMBUSTION OF HETEROGENEOUS POLYDISPERSE PROPELLANTS - EFFECTS OF ADDITIVES: R. L. Glick; Thiokol Corporation
1600	-	NITRAMINE SMOKELESS PROPELLANT RESEARCH: Leon D. Strand and Norman S. Cohen; Jet Propulsion Laboratory
1630	-	COMBUSTION RESPONSE MODELING FOR COMPOSITE SOLID PROPELLANTS: N. Cohen, N. Ramohalli, L. Strand and F. Culick; Jet Propulsion Laboratory
1700	-	ADJOURN

*It is essential that the meeting room be cleared by 1130 in order to make room for another function being held at the Antelope Valley Inn.

Thusday
10 Mar 77

0800	-	REGISTRATION
0830	-	T-BURNER VENT LOSSES: S. Murthy, J. Osborn and J. Renie; Purdue University
0900	-	DETERMINATION OF THE ADMITTANCES OF BURNING SOLID PROPELLANTS BY THE DRIVEN BURNER TUBE METHOD: B. T. Zinn, M. Salikuddin and B. R. Daniel; Georgia Tech
0930	-	HOLOGRAPHY OF SOLID PROPELLANT COMBUSTION: R. F. Wuerker and R. A. Briones; TRW Defense and Space Systems Group
1000	-	COFFEE BREAK
1030	-	AUDIBLE AND ULTRASONIC EMISSIONS FROM COMPOSITE SOLID PROPELLANTS: James I. Craig and Warren C. Strahle; Georgia Tech
1100	-	EVALUATION AND COMPILATION OF THE THERMODYNAMIC PROPERTIES OF HIGH TEMPERATURE SPECIES: Malcolm W. Chase; Dow Chemical
1130	-	HYBRID FINITE ELEMENT MODELS FOR FRACTURE ANALYSIS: S. Atluri, K. Kathiresan and M. Nakagaki; Georgia Tech
1200	-	LUNCH
1330	-	MATERIALS WITH VARIABLE BONDING: M. Quinlan; AFRPL
1400	-	LATTICE DYNAMICS OF HEATED HMX: T. Brill and F. Goetz; University of Delaware
1430	-	BREAK
1500	-	HMX THERMAL DECOMPOSITION: B. Goshgarian; AFRPL
1530	-	SYNTHESIS OF NITROPOLYMERS: F. Myers; AFRPL
1600	-	SYNTHESIS OF BURN RATE MODIFYING ADDITIVES: I. Mishra; AFRPL
1630	-	CHEMISTRY OF CURING AND AGING OF PROPELLANTS: N. Viswanathan; AFRPL
1700	-	ADJOURN

Friday
11 Mar 77

0800 - REGISTRATION

0830 - STUDY OF THE CONSEQUENCES OF THE FLOW OF HIGH-PRESSURE, HIGH-TEMPERATURE GASES INTO PROPELLANT CRACKS: A. Takata and A. Wiedermann; IIT Research Institute

0900 - MODELING THE DEFLAGRATION-TO-DETONATION TRANSITION IN REACTIVE SOLID PARTICLE-GAS MIXTURES: Herman Krier; University of Illinois at Urbana-Champaign

0930 - DEFLAGRATION TO DETONATION TRANSITION IN HMX-BASED PROPELLANTS: M. Cowperthwaite and J. Rosenberg; Stanford Research Institute

1000 - COFFEE BREAK

1030 - ANALYSIS OF THE COMBUSTION-TURBULENCE INTERACTION ON AN EROSIVELY-BURNING SOLID PROPELLANT: R. Beddini, A. Varma and E. Fishburne; Aeronautical Research Associates of Princeton

1100 - THEORETICAL AND EXPERIMENTAL INVESTIGATION OF EROSIVE BURNING OF NON-METALLIZED COMPOSITE SOLID PROPELLANTS: K. Kuo, M. Razdan and R. Kovalcin; Penn State University

1130 - STUDY OF EROSIVE BURNING PHENOMENA IN COMPOSITE PROPELLANTS: Merrill K. King; Atlantic Research Corporation

1200 - BEHAVIOR OF ALUMINUM IN COMBUSTION OF SOLID ROCKET PROPELLANTS: E. Price and R. Sigman; Georgia Tech

1230 - HYDRAZINE DECOMPOSITION FOR MONOPROPELLANT PROPULSION SYSTEMS: A. C. Baldwin, D. M. Golden, K. Lewis, R. T. Rewick and H. Wise; Stanford Research Institute

1300 - HYDRAZINE ELECTROCHEMICAL STUDIES: H. Martens; AFRPL

1330 - ADJOURN

AFRPL ACTIVITIES ASSOCIATED WITH THE DEVELOPMENT OF ELECTRIC SPACE THRUSTERS: TECHNOLOGY NEEDS AND RESEARCH REQUIREMENTS

Captain Gregory Engelbreit
and
Lieutenant Sharon Pruitt

AFRPL/LKDA Edwards AFB, California

In anticipation of future Air Force secondary propulsion requirements, the Air Force Rocket Propulsion Laboratory (AFRPL) has actively supported the development of low thrust electrical propulsion devices since 1971. The requirement for performing large total impulse (greater than 40 thousand lb sec) secondary propulsion missions with minimum weight and high reliability makes simple electric propulsion devices attractive. This presentation will outline the AFRPL's current and planned electric propulsion programs. Required areas of research to further electric propulsion growth (such as high thrust) will be identified.

The AFRPL presently has an exploratory effort in the development of a one millipound thrust electric propulsion device known as the solid Teflon pulse plasma thruster. The current status of this 6.2 effort will be presented as well as the planned flight hardware development program. Those technology areas that require more data for a deeper understanding of engine operation will be discussed.

PARTICLE INTERACTIONS IN COLLOID EXHAUST PLUMES AND EFFECTS OF A DISTRIBUTION OF DROPLET SIZES

Julius Perel and John F. Mahoney

Phrasor Technology
Pasadena, California 91101

This program is directed toward the understanding of the basic colloid thruster generation and acceleration process and the cause of performance degradation. This thruster is considered applicable for attitude control and station keeping on future Air Force satellite missions. The program involves a theoretical investigation of the process of droplet emission to determine the source of negative ion production causing sputter erosion of the emitter. The experimental part of the program is aimed toward the verification of negative ion production.

A model of emitter tip erosion has been developed that correlates with performance degradation. The erosion is caused by back bombardment of the emitter by negative ions produced from the break up of slow droplets as a result of collisions with fast ions. The calculations are made assuming the droplets are all the same size rather than using the distribution of droplet sizes actually observed. If at least one negative ion is produced at each ion/droplet collision the resulting sputtering rate is sufficient to explain the measured erosion.

The recent investigations have been devoted to the effects of including a distribution of droplet sizes in the analysis. A normal distribution of the charge-to-mass ratio was chosen with a standard deviation of about one third of a mean charge-to-mass ratio of 10^4 coul/kg. This approximates the distribution observed experimentally. Results of the analysis shows that the calculated collision ratio increases when the droplet population is changed from uniform size to the assumed distribution. The effects of varying the distribution were examined by changing the standard deviation and by replacing the normal distribution by an unsymmetrical distribution. Results and techniques will be presented.

PLASMA ACCELERATION IN PULSED ABLATIVE ARC DISCHARGES

Dominic J. Palumbo and Martin Begun

Fairchild Republic Company

Current Air Force requirements call for a low thrust, high specific impulse propulsion system having large total impulse capability to perform such satellite functions as north-south stationkeeping, low altitude drag compensation, and attitude control. The need for such a device has precipitated AFRPL hardware development of millipound pulsed plasma thrusters using solid tetrafluoroethylene (Teflon) propellant over the past four years. The objective of the basic research program being reported upon here has been to support these developmental efforts by providing both physical understanding and analytic modelling of the acceleration process in pulsed ablative thrusters. This program could provide the inputs necessary to improve propulsive efficiency and characterize the plume produced by this device. A three year program was carried out in which the continuum MHD equations and a second order accurate explicit numerical integration scheme were used to mathematically model the plasma dynamics in pulsed ablative plasma accelerators with parallel rail electrodes. Concurrent with these analytic efforts an experimental diagnostics program was performed utilizing high speed photography, magnetic fluxprobes, time of arrival probes, Rogowski coils, and Langmuir probes to obtain a detailed two dimensional picture of the plasma acceleration as a function of time. Measurements of magnetic flux density, current density, plasma velocity, and, most recently, electron number density and temperature provided a basis for comparison of the computed flow fields to the actual physical event. The major portion of this presentation will deal with the results of our attempt to analytically describe the evolution and acceleration of plasma produced by depolymerization of the solid Teflon propellant. Details concerning the unique difficulties associated with this particular problem and measures taken to circumvent numerical instabilities will be discussed. Results of the calculations and comparison to the experimentally diagnosed flow field will be presented.

MECHANICS OF MAGNETOPLASMADYNAMIC ARC JETS ACCELERATION PROCESSING*

Gordon L. Cann and Adriano C. Ducati

Technion, Inc
Irvine, CA

The ability to utilize the air at altitudes of from 100 to 250 miles as propellant for an axisymmetric plasma accelerator is being investigated under this contract. Several modes of operation can be postulated for an accelerator comprising a moderately strong solenoidal magnetic field superposed over a cylindrical anode and a central thermionic cathode:

1. Electromagnetic forces caused thermionic electrons to fill a large volume of space downstream of the electrode. Ions can be formed by collisions between these electrons and ambient atoms. These ions are accelerated through the potential drop between the electrode, collect thermionic electrons and leave the system with both axial and azimuthal momentum, imparting spin and thrust forces to the magnet coil. If ions are present in the environment through which the accelerator is passing, these may also be captured and accelerated out of the system.
2. The potential can be high enough so that electrons emitted by the cathode can be accelerated across the magnetic field to bombard the anode. These high energy electrons can desorb atoms and/or ions from the adsorbed surface layers. The ions can be accelerated as in (1) above. If enough atoms are desorbed, then volume collisions between them and high energy electrons can produce more ions. This process may eventually lead to breakdown, at which point it would operate as a conventional pulse MHD accelerator.

Experiments to date have been limited primarily to operation in mode 2, ie, use of adsorbed gases on the electrode and other component surfaces. Extensive experiments have been conducted in both large and small vacuum facilities over pressures ranging from 10^{-8} torr to over 10^{-3} torr.

The ion production processes and efficiencies have been intensively studied during the current phase of the program. Several pieces of equipment were designed specifically for studying the efficiency of ion production. Data obtained from this equipment indicated that ions were produced on the surface of the anode by inelastic collision with electrons emitted from the thermionic cathodes. The ion current obtained by collecting these ions on the center electrode was measured to be about 500 times smaller than the electron current required to produce the ions.

PULSED PLASMA ACCELERATION IN STRONG BIAS MAGNETIC FIELDS FOR ELECTRIC PROPULSION APPLICATION

C. L. Dailey

TRW Systems
Redondo Beach, Calif.

Pulsed plasma thrusters are a weight-effective method of meeting low thrust, high impulse, mission requirements for Air Force spacecraft in which high specific impulse is used to reduce the propellant mass needed for a given impulse. Past work at TRW Systems, under AFOSR support, has shown that 1) plasma acceleration by self-fields alone cannot be efficient, 2) high efficiency can be achieved by applying a strong bias magnetic field perpendicular to both the current flow and acceleration directions and 3) this approach is feasible only in a jxB channel.

In the present accelerator a bias field decreasing in the flow direction overcomes the 50% upper limit on efficiency that is imposed in a rectilinear channel having a constant bias field. The accelerator channel is about 1 inch long by 1 inch high by 1 inch wide. Shaped magnet pole pieces are used to decrease the bias field from 8000 Gauss at the channel inlet to 1500 Gauss at the exit, while a constant electric field is applied between parallel electrode plates. A practical thruster would use a pulsed injection valve to introduce a storable gaseous propellant (e.g. xenon or some form of propellant decomposition products) into the accelerator channel during the discharge period of a pulse-line energy storage bank. The present work is being done with a pulsed current discharge during a steady gas flow.

The bias magnet is suspended as a ballistic pendulum whose deflection indicates the impulse developed by the electromagnetic force. Except for the drag effect of the channel walls, this impulse is equal to that delivered to the plasma. Data obtained in this way have produced thruster efficiencies greater than 100%, indicating that the wall drag is not ignorable and/or that more mass is expelled per discharge than that supplied by the gas flow. The plasma momentum has been measured by an impulse pendulum in the vacuum chamber. This impulse has been found to be only slightly less than that of the magnet, again indicating more than 100% efficiency. This result shows that additional mass enters the discharge, possibly by electrode ablation. A preliminary check on this possibility was made by covering the cathode with a glass sheet except for an 0.2 inch wide gap at the center. This had no effect on the measured plasma impulse. Further diagnostic tests will be made in an effort to understand the discharge and the acceleration process. It is concluded from the present results that the wall drag effect is not serious and it appears that the bias field does produce efficient acceleration.

KINETICS OF METAL OXIDE FORMATION

Dr. David M. Mann

Air Force Rocket Propulsion Laboratory
Edwards AFB CA 93523

Metals, particularly aluminum, are added to solid propellants in high concentrations to improve combustion stability and motor performance. Oxides of these metals, produced during propellant combustion, form particulates which, in the exhaust plume, are largely responsible for the plume signature in the visible and near-infrared spectral regions. Modeling of particulate produced signatures is seriously hampered by the scarcity of information on particulate formation. The objective of this program is to investigate the kinetics of metal oxidation and subsequent particle formation for the prediction, and possible control, of plume particulate sizes.

This work will focus on gas phase oxidation and particulate formation mechanisms. The approach taken is to react metal vapor (initially aluminum) and oxygen in a flowing system to provide spatial and temporal separation of reaction products. Time evolution of metal oxide species, as monitored by mass spectrometric and spectroscopic techniques, will be used with an appropriate kinetic model to identify a mechanism of particulate formation. Effects of added species normally encountered in combustion (e.g. H, F, Cℓ, OH, etc.) will also be studied.

PARTICLE OPTICAL PROPERTIES MEASUREMENTS (POPM) PROGRAM

J. M. Dowling and C. M. Randall

Ivan A. Getting Laboratories
The Aerospace Corporation
El Segundo, California

A significant portion of the infrared signature of a rocket plume is determined by the optical properties of the particles present in the plume. Predicting the radiation from such plumes for systems analysis purposes requires accurate and detailed knowledge of the optical properties of the particles occurring naturally, or as products of combustion, or intentionally placed in the rocket exhaust.

The objective of the POPM program is to ascertain the reliability with which the thermal radiative characteristics of hot particles can be predicted by calculations based on refractive indices characteristic of large samples. The program involves two experimental efforts. The first is to measure the required refractive indices at high temperature, from which emissivities of particles have been predicted, and the second is to measure the spectral radiance of a single isolated heated particles.

Reflectivity spectra of Al_2O_3, MgO, and ZrO_2 were obtained at room and elevated temperatures. Carbon data were also obtained at room temperature. The reflectivity data were analyzed to yield the complex index of refraction of the materials in the infrared region $\lambda = 25$ to $\sim 4\mu m$. The expected emissivity of micron-sized particles of all of the above materials has been computed (using Mie theory) for the spectral interval 25 to 5.5μm for spherical particle sizes in the range 0.5 to 50μm. It is concluded that the emissivity of small particles cannot always be reliably computed from refractive index data, because of the critical dependence of the emissivity on particle size and refractive index spectrum. Examples to illustrate these points will be presented.

A description of the single particle emissivity experiment will be given. Problem areas encountered in this difficult experiment and progress made to date will be discussed.

SHOCK TUBE MEASUREMENTS OF MOLECULAR BAND STRENGTHS ASSOCIATED WITH BORON PROPELLANTS

Anthony L. Russo and Donald W. Boyer
Calspan Corporation

Abstract

Experiments are being conducted in a high-purity shock tube in which the equilibrium thermodynamic state of a boron fuel (B_2H_6), oxidizer, and diluent (argon) mixture can be varied. A novel, scanning, infrared spectrometer is used to identify the important radiant molecular species in the short wave infrared region (SWIR) from about 1 to 5.5 μm. The relative concentration of the radiatively dominant species is then optimized by varying the test gas mixture and shocked gas conditions. The infrared spectrometer is then used to measure the band strength of the selected species. This paper describes the experimental technique and the scanning, infrared spectrometer.

Initial experiments were conducted for a $B_2H_6/O_2/Ar$ mixture. The results of these experiments indicate that HBO_2 near 5 μm is the dominant radiator in the 1-5.5 μm spectral region. The experiments indicate that the radiation intensity from the HBO_2 scales properly with variations in the predicted number density from computer calculations.

Experiments for calibration purposes are currently being conducted using CO_2, whose band strengths are well documented, and using H_2O, in order to permit the measurement of the HBO_2 band strength near 2.7 μm. Experiments are also planned to study the BH_x system using diborane and argon diluent. These experiments and the results of the band strength measurements will be discussed.

LASER FLUORESCENCE MEASUREMENTS OF VIBRATIONAL ENERGY TRANSFER IN WATER AND AMMONIA

F.E. Hovis, J. Finzi and C. Bradley Moore

University of California, Department of Chemistry
Berkeley, CA 94720

Water vapor is an extremely efficient vibrational energy relaxer, both with itself and with other molecules. Thus, besides being a problem of fundamental interest in chemical kinetics, relaxation rates of water are important in determining the gas dynamics of and the radiation emitted by many combustion systems, particularly exhaust plumes from airborn vehicles.

In a set of experiments done on vibrational energy transfer, a Nd-YAG pumped optical parametric oscillator provides a coherent source of tunable infrared radiation which is used to excite either the symmetric (100) or asymmetric (001) stretch of $H_2{}^{18}O$. By an appropriate choice of interference filters and gas filter cells, fluorescence from the stretching levels, the bending overtone level (020), or the bending overtone and fundamental (010) levels combined may be observed. The resulting signal-averaged fluorescence traces have been analyzed to give the total deactivation rate constants for the stretching, bending overtone, and bending fundamental levels. A set of experiments is also done using argon as a collision partner.

Analysis of the (001) fluorescence shows that (001) and (100) are coupled and relax together with a rate constant $k_s = (7.4 \pm .7) \times 10^6\ sec^{-1}\ torr^{-1}$. Argon is found to be about 200 times less effective in deactivating the stretches. A similar analysis of (020) fluorescence gives a rate constant for deactivation of $k_2 = (3.0 \pm .4) \times 10^6\ sec^{-1}\ torr^{-1}$, with argon again being about 200 less effective. The decay of fluorescence from the (020) and (010) levels together gives limits on the deactivation rate constant for the (010) level of $1.8 \times 10^6\ sec^{-1}\ torr^{-1} < k_1 < 3.0 \times 10^6\ sec^{-1}\ torr^{-1}$.

By comparing the relative total fluorescence from (010) and (020), it is possible to extract some qualitative information on branching ratios. It is found that the deactivation of (020) has significant contribution from both the near-resonant process $H_2O(020) + H_2O(000) \rightarrow 2H_2O(010)$ and the V $\rightarrow$ T,R process $H_2O(020) + H_2O(000) \rightarrow H_2O(010) + H_2O(000)$. In addition, it is concluded that in stretching level deactivation, the channel going to (020) predominates.

Future experiments on deactivation of $H_2{}^{16}O$ require the higher laser powers which will be provided by a new parametric oscillator system that will be completed within the next few months. Relaxation of the bending vibration of NH_3 will be studied in the intervening time using a CO_2 TEA laser.

KINETIC REACTION COEFFICIENTS IN ROCKET EXHAUST PLUMES

W. Snow, L. Schearer, K. Nygaard and R. Corbin

University of Missouri
Rolla, MO

Abstract not submitted for publication.

Translational Excitation of CO_2 to a Radiating State

Subbarao Ryali and J. B. Fenn - Yale University
C. E. Kolb - AeroDyne Research, Inc.

We have recently achieved some modest success in determining cross sections for excitation of ground state H_2O and CO_2 molecules to radiating states by collisions with themselves or with other molecules at translational energies in the several eV range. The idea is that two opposed free jets are set far enough apart so that they comprise in effect two uncollimated molecular beams. Their molecules thus encounter each other in an interaction region where the densities are so low that each molecule in one of the jet flows undergoes at most a single collision with a molecule from the opposed jet flow. By aerodynamic acceleration with hydrogen or helium and control over the source temperature the effective center of mass collision energies can be varied over a fairly wide range. A sensitive infrared detector "looks" at the interaction region and responds to photons radiated from molecules which have been collisionally excited.

We use two axisymmetric sonic nozzles which are 100 microns in diameter. They are positioned 9 cm apart in a chamber which is 80 cm in diameter and 100 cm long, evacuated by an oil diffusion pump 80 cm in diameter. The nominal pumping speed of 3×10^4 liters per second is halved by a freon cooled baffle. The pumping speed is such that we can use source pressures up to 1500 torr while maintaining background pressure at a few times 10^{-5} torr. The detector is a high impedance photovoltaic chip of Indium Antimonide (InSb), .04 cm^2 in area. A silicon lens with a transmission of 0.21 focusses the radiation on the detector from a collision volume of about one cubic centimeter. The flow from one of the nozzles is chopped at a frequency of 200 hertz in order to take advantage of increased signal-to-noise provided by tuned amplifiers and phase sensitive detection. The detector and all the surfaces which it sees are cooled to liquid nitrogen temperatures.

For the asymmetric stretch mode of CO_2, the photon wavelength is 4.3 microns corresponding to a threshold energy of 0.288 eV. For this wavelength, the overall response of the detection system, including the amplifiers, is 2.48×10^9 volts/watt. The noise is such that we can achieve an effective output sensitivity of about one millivolt corresponding to an input of 4×10^{-13} watts. Under these conditions, we have been able to detect radiation from CO_2 excited by collisions with H_2, N_2, CO_2 and Ar molecules. A preliminary analysis of the data indicates that the excitation cross sections range from perhaps 0.1 to 10 $\mathring{A}^2$ depending upon the identity of the collision partners and the collision energy.

ANALYTICAL INVESTIGATION OF MULTINOZZLE PLUME FLOW FIELDS/
Contract No. F44620-76-C-0021

Stanley Rudman

Grumman Aerospace Corporation
Research Department
Bethpage, New York 11714

There are many phenomenon associated with the flow field created by the exhaust of jet and rocket engines which are of prime importance to many Air Force space and aircraft programs. Plume fluid mechanics must be well understood so that advanced Air Force systems designed on the basis of predictions can accomplish their goals in the areas of detection, surveillance and intelligence. Primary interest is in the exhaust plume as a source of infrared (IR) and electromagnetic (radar cross section) observables. A detailed description of the thermodynamic and chemical properties of the flow field is the basis of the calculation of these observables. The required distributions of chemical species, pressures and temperatures are governed by the plume fluid mechanics. Many vehicles of interest have multiple nozzle resulting in interacting plumes. These flow fields are complex three dimensional supersonic flows with many shock waves and discontinuity surfaces and cannot be computed with present numerical schemes.

The present work is aimed at developing an advanced numerical technique which will predict the inviscid structure of the multiple plume. This is a finite difference computational scheme which incorporates discrete discrete fitted shocks, slip surfaces and more complex discontinuities. The finite difference cell containing the impingent shock intersection with the plume boundary inserts the centered expansion at that point of intersection. The discontinuities and singularities float through the three dimensional mesh network and while the resulting computer logic is quite complex the generality of the program is great. The initial computational results for the impingement of two uniform rectangular cross section plumes will be presented.

Regions of subsonic flow arise in the plume flow field as a result of Mach discs. There is no existing program which integrate the flow field past the sonic throat associated with the Mach disc flow. An analysis will be presented which accounts for pressure and viscous mixing forces which passes smoothly through the throat.

PHYSICAL/CHEMICAL PROCESSES CONTROLLING LOW ALTITUDE ROCKET EXHAUST PLUME VISIBILITY

Roger D. Thorpe

AeroChem Research Labs., Inc., Princeton, NJ

The problem of visible exhaust plumes has created a need for the Air Force to develop propellants which minimize these signatures. This research program is directed toward elucidating, through the use of applicable flow models, the physical and chemical processes that control visible signatures of low altitude afterburning exhaust plumes, with emphasis placed on primary smoke and primary/secondary smoke interactions. Crucial to the success of plume visibility models is an accurate determination of the primary smoke properties at the nozzle exit plane. The current work concentrates on determining the sensitivity of predicted particle and gas properties to uncertainties in assumptions concerning (i) particle sizes and number densities and (ii) theoretical particle/gas coupling parameters. Future work will be directed at studying primary smoke formation mechanisms in the chamber and nozzle and performing needed research on secondary smoke production mechanisms such as heterogeneous nucleation, particle coagulation and the effects of chemical kinetics and diffusion on particle growth.

NONEQUILIBRIUM PROPERTIES OF EXHAUST PLUMES

M. Branch

University of Colorado
Boulder, CO

Abstract not submitted for publication.

UNSTEADY PLUME MODELING FOR HIGH ACCELERATION ROCKET LAUNCH

John I. Erdos

General Applied Science Laboratories, Inc.
Westbury, New York 11590

Unsteady plume effects are produced by impingement of the steady, supersonic exhaust plume on the ground surface, producing a blast-like flow field. The rate of energy deposition at the origin of the blast field provides the principal scaling parameter for the overall structural features of the inviscid field. This parameter has been characterized in terms of vehicle thrust, specific impluse, lift-off weight and nozzle exit area for an inviscid, steady exhaust plume. It is demonstrated that very high acceleration at lift-off produces an essentially "explosive" deposition of energy at ground level, whereas very low acceleration produces a virtually constant rate of energy deposition. However, turbulent mixing reduces the effective energy deposition rate (for low or moderate acceleration rates) by entraining low energy (ambient) air into the plume. Assessment of the magnitude of this reduction is currently being carried out for a representative launch vehicle. Numerical results will be presented for this example, and scaling to other launch conditions will be discussed.

CONDENSATION AND PARTICLES IN EXHAUST PLUMES

J. W. L. Lewis and W. D. Williams

ARO, Inc.
Arnold Air Force Station, Tennessee

The occurrence of both homogeneous and heterogeneous condensation processes in rocket exhaust plumes is of significance for the prediction of the scattering of radiation by the plume, the production and deposition of contaminants on adjacent surfaces and the characterization of the flowfield itself. The initial goal of this work has been to characterize the homogeneous condensation processes in vacuum plume expansions and determine the appropriate scaling laws for condensation onset, growth rate and cluster size as a function of gas source and species parameters. Laser Rayleigh and Raman scattering have been employed to study the expansions of single gases from sonic orifices and conical nozzles. The scaling laws obtained for such expansions will be presented, and the use of the Lennard-Jones 12:6 potential well-depth and range parameters as scaling parameters will be discussed.

During the current fiscal year the same experimental techniques have been used to study the exhaust plume of a 0.1 lbf monopropellant hydrazine thruster, and the results obtained to date will be presented in part.

CREATION AND DESTRUCTION OF VIBRATIONALLY EXCITED OH

Glenn C. Light

Ivan A. Getting Laboratories
The Aerospace Corporation
El Segundo, California

Measurement of the rates of the chemical reactions, $O(^3P) + H_2(v=1) \xrightarrow{k_0, k_1} OH(v=0, 1) + H$, is reported here for the first time. The effect of vibrational energy in the reactant species in promoting a particular chemical reaction is an issue of fundamental interest in chemical kinetics generally, and to the military in particular. The distribution of internal energy in the products of such a reaction is of practical importance in molecular lasers and in gas dynamics. The creation and removal rates of vibrationally excited OH are especially important in determining the chemical dynamics and radiation emitted from most combustion processes including rocket exhaust plumes.

The measurements were conducted in a laboratory flow tube apparatus at room temperature. The O-atoms were generated by the reaction, $N + NO \rightarrow N_2 + O$. Vibrationally excited hydrogen was created on a hot tungsten filament. Absolute number density of product OH(v) was measured by calibrated laser induced fluorescence using a frequency doubled tunable dye laser.

Data were generated for the dependence of OH(0, 1) densities on NO flux and on $H_2(1)$ density. Interpretation of the data was aided by nonequilibrium kinetics computer model calculations. The inferred rate constant, $(k_0 + k_1)$, is less than the previously reported[1] upper limit. The branching ratio (k_1/k_0), is also measured. Numerical values will be presented.

Limiting values are obtained for several other processes involving OH(v=0, 1) from these experiments, namely:

$$
\begin{aligned}
O + H_2(1) &\rightarrow O + H_2(0) \\
O + H_2(0) &\rightarrow OH(1) + H \\
OH(0) + H_2(1) &\rightarrow H_2O + H \\
OH(1) + H_2(1) &\rightarrow H_2O + H \\
OH(1) + N &\rightarrow OH(0) + N \\
OH(1) + N &\rightarrow NO + H
\end{aligned}
$$

The importance of these results for high altitude missile plume modeling is discussed in detail.

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1. J. H. Birely, J. V. V. Kasper, F. Hai and L. A. Darnton, Chem. Phys. Lett. 31, No. 2, pgs 220-224, 1 March (1975).

THE AFRPL BASIC RESEARCH PROGRAM

Lawrence P. Quinn

AFRPL/XP (Plans Office)
Edwards AFB, CA 93523

AFRPL was recently authorized to develop and execute a 6.1 basic research program. This discussion will provide an overview of that program. The magnitude of the program and program organization will be discussed from several aspects. The relationship of this effort to the 6.2 program will be defined as well as the rocket propulsion research needs. A detailed discussion of the FY-77 program will concentrate on those efforts not being reviewed at this meeting. The talk will conclude with a definition of how others may get involved in the program.

ARMY COMBUSTION RESEARCH

Carl W. Nelson

U. S. Army Ballistic Research Laboratory
Aberdeen Proving Ground, Maryland 21005

This paper outlines the Army program for basic research in combustion mechanisms for guns which differ from rockets mainly by a completely transient pressure field and an absence of perchlorate oxidizers.

Research is sponsored by two agencies; BRL manages a mostly in-house program and the Army Research Office awards grants to mostly universities. The BRL program is the more applied. The in-house program has two thrusts (1) the influence of pressure, pressurization rate, initial temperature, and composition on the instantaneous regression rate and (2) microscopic physical and chemical processes.

Both measurement and prediction of transient burning rates are sought, particularly at low pressures (less than 30MPa) and high pressurization rates (100MPa/ms) because these rates affect the flame spreading through the granular bed. Research is also needed on burning rate sensitivity to initial temperature, erosive burning in the grain perforations, and burning behavior at high pressures (400-1000MPa). On the microscopic scale we are presently investigating CAR spectroscopy, flame chemistry, and pressure dependence of reactions. Research is needed on flame chemistry and solid pyrolysis mechanisms. Although most present gun propellants are homogeneous nitrocellulose based, there is interest in nitramine composites, and high burning rate formulations of the Hivelite type.

On the next higher scale of gun combustion, research is needed on the behavior of the burning mobile granular bed. Particularly needed are experiments on bed rheology, particle drag, local combustion rate, and flame spreading. We have emphasized modeling of the process for the past few years and now need useful experimental data for model variation and correction.

NAVY RESEARCH IN SOLID PROPELLANT COMBUSTION

R. Derr

Naval Weapons Center
China Lake, CA

This talk will review fundamental and applied research programs being conducted by the Navy and under Navy sponsorship in the area of solid propellants. Specific details will be given to selected programs being conducted at the Naval Weapons Center. In addition, areas of technical interaction between the Navy and the Air Force will be identified.

UNSTEADY PROCESSES IN SOLID PROPELLANT COMBUSTION

A. Crespo & M. Kindelán

INSTITUTO NACIONAL DE TECNICA AEROESPACIAL "ESTEBAN TERRADAS"

Paseo Pintor Rosales 34, Madrid-8, Spain

The purpose of this work is to develop a theoretical analysis of unsteady processes in solid propellant combustion, particularly combustion stability and extinction by rapid depressurization. The interest in understanding combustion stability stems from the fact that it may lead to inefficient operation in rocket motors. Extinction by depressurization is of interest in order to design rocket engines for space application with stop-restart capability.

It is assumed that the solid decomposes at its surface by a pyrolysis law, and the gaseous decomposition products react exothermically following an Arrhenius law. The nondimensional activation energy of the gas phase reaction is considered to be large so that the reaction takes place in a thin zone where the temperature is close to the flame temperature.

The gas phase is assumed to be quasisteady and under this condition the equations in the gas phase are solved in the limit of high activation energies yielding conditions for the burning rate and heat flux to the solid. The analysis of the energy equation in the condensed phase shows that the characteristic response time of the solid to gas phase perturbations is large compared to the characteristic residence time in the heat-up zone of the solid, their ratio being of the order of the nondimensional activation energy in the gas phase reaction. A stability criterion has been obtained, resulting that for large values of the nondimensional activation energy of the pyrolysis law there is always unstable behaviour. For the stable case the dynamic extinction problem is being presently investigated. Preliminary results seem to give an extinction criteria for step-like pressure changes.

Future work will include heat losses and will calculate higher order terms in the high activation energy limit. Possible retention of unsteady effects in the gas phase is also contemplated.

RECENT RESEARCH ACTIVITY AT ONERA ON
COMBUSTION INSTABILITY AND EROSIVE BURNING

Paul Kuentzmann and Paul Lengelle

Office National d'Etudes et de Recherches Aérospatiales
(ONERA)
92320 Chatillon (France)

Combustion instabilities in large solid composite propellant motors are not yet fully understood and ONERA is carrying out experimental studies both to characterize the overall phenomena and to determine the propellant response to pressure and velocity oscillations, as well as fundamental researches in order to reach a better prediction of the motor stability or of the instability levels.

The experimental studies of the motor natural instabilities have concerned for several years new machined grain geometries, which have required departures from standard approaches to the problem; test runs on a scaled down motor give a satisfactory answer for the determination of the potentially unstable modes and also provide information on the mechanisms of the phenomenon. The response of solid propellants to pressure oscillations is measured by means of the modulated exhaust motor technique; in spite of the many improvements in this technique, the precision of the results remains very sensitive to the quality of the measurements. A motor designed for the determination of the response of solid propellants to pressure and external flow velocity oscillations is being used; the interpretation of the measurements remains however to be done. These various experimental techniques have required efforts on the methods of measurement.

The analysis of the phenomena has been mostly devoted so far to the interpretation of the results obtained with the motors used to determine the response of solid propellants. More recently the setting up of a numerical program has been started, the aim being to predict the non stationary operating of a simple geometry motor; this study, which relies on numerical techniques, will be extended if possible to more elaborate geometries.

Erosive combustion has not been investigated as thoroughly as combustion instabilities. Three types of activities have been pursued: the experimental investigation of the erosive response of plateau composite propellants, the modelling of the erosive effect on a composite propellant with a view to identifying the mechanisms responsible for it, various experimental activities on erosive combustion related to more general studies.

ROTATING VALVE FOR VELOCITY COUPLED COMBUSTION RESPONSE STUDIES

R. S. Brown, P. G. Willoughby, and V. L. Kelly

Chemical Systems Division, United Technologies, Sunnyvale, CA

The combustion response characterizations of solid propellants are important factors which determine the combustion stability of solid propellant rocket motors. Recently Chemical Systems Division (CSD) has conducted two programs under contract to AFRPL to develop and demonstrate the rotating valve method of measuring the pressure coupled combustion response of solid propellants. This device consists of a small rocket motor attached to a rotating valve assembly. The valve produces controlled throat area oscillations thereby generating small amplitude pressure oscillations which depend in part on the combustion response.

Measurements have been made using both aluminized and nonaluminized propellant formulations. The results show good agreement with T-burner measurements when the T-burner vent term is taken to be zero. In addition, reproducible apparatus operation has been demonstrated for frequencies between 80 and 800 Hz and for combustion pressures up to 1,500 psi with propellants containing as much as 18% aluminum. The results of these studies substantiate the use of the rotating valve apparatus for measuring the pressure-coupled combustion response of both aluminized and nonaluminized propellants.

The value of the rotating valve apparatus is not limited, however, to the measurement of pressure-coupled combustion response functions. Recent studies conducted at CSD under IR&D suggest the rotating valve can be adapted to the measurement of velocity-coupled response functions. Velocity oscillations of controlled frequency and amplitude can be generated in the test motor by simultaneously operating rotating valves at each end of the motor, 180° out of phase. Analysis of this configuration shows the generated pressure oscillations result mainly from velocity coupling effects and with pressure coupling having only a minor effect. Therefore, the rotating valve method offers the potential for experimentally investigating many characteristics of velocity coupling which have been postulated by purely analytical arguments.

Under contract to AFOSR CSD is investigating the applicability of the two-valve approach for measuring velocity coupling responses. The program will consist of analytical studies to improve the accuracy of the transient ballistics model, to explore its limitations, and to estimate the effects of experimental uncertainties; concurrent experimental studies include construction of the apparatus, comparison of its performance with predictions under cold flow conditions, and assessing the apparatus performance and appropriateness for conducting combustion tests. If the results are positive, this technique will provide a method for conducting detailed studies of the velocity coupling process, the mechanisms and parameters influencing this process, and its relationship to mean burning rate shifts and erosive burning.

RESEARCH ON UNSTEADY COMBUSTION PROCESSES

Leonard H. Caveny, Michael M. Micci, Alon Gany, and Martin Summerfield

Aerospace and Mechanical Sciences Department
Princeton University
Princeton, New Jersey

Velocity and Pressure Coupling in Solid Rockets

A methodology centered around the modulated throat rocket motor (MTRM) is being developed to investigate the dynamic responses of high performance rocket motors in which longitudinal mode combustion instability are a consideration. The primary objective is to develop a means of directly ranking the susceptibility of candidate propellants (specifically in terms of small changes in formulation) to the several types of interactions that lead to rocket motor instabilities. The experimental rocket motors have high loading densities and are not specially devised apparatuses for testing propellants isolated from the rocket motor chamber environment. During the last year, the data analysis procedures have been refined to a point that gains and losses can be measured as a function of excitation frequency and Mach number.

Aluminum Burning in Solid Rockets

The combustion of aluminized propellants under the cross-flow conditions that exist in rocket motors are being studied to answer questions that have been raised concerning metal agglomerate particle size (an important consideration in rocket motor combustion efficiency and damping of acoustic waves). High-speed photographs (∿ 2000 fr/sec) were taken of the aluminum oxide agglomerates forming on the surface, moving along the surface, entering the flow field, and in the flow field. For the aluminized double base propellants studied, the agglomerates ignite on the surface. After ignition, agglomerate behavior can be divided into several stages (depending on the port flow condition); agglomerates continue to grow while remaining in one location, they grow by rolling around on the surface (either with or against the direction of flow), and they grow by colliding with other particles. There appears to be an adhesion effect of the surface resisting lift-off forces. The agglomerate dimensions vary inversely with port mass flux and are influenced to a lesser extent by burning rate. The mean diameter of the agglomerates decreases with increasing pressure. The time for an agglomerate to leave the surface varies inversely with port mass flux. The agglomerates are larger than anticipated (about 95% of the mass contained in agglomerates 300 to 400 μm). No evidence of agglomerate break-up has been observed for cross-flow velocities less than 100 m/sec.

TITLE: Combustion of Heterogeneous Polydisperse Propellants - Effects of Additives

SPEAKER: R. L. Glick

ORGANIZATION: Thiokol Corporation

ABSTRACT: The combustion model developed in previous work has been employed to correlate the effect of iron oxide catalyst on rate/pressure behavior. For these calculations it has been assumed that iron oxide is chemically inert and sufficiently small that it exists in fixed proportion to the binder. The iron oxide is assumed to reduce the activation energy of the gas phase reactions. Correlations of Miller, et al.'s data are very promising.

NITRAMINE SMOKELESS PROPELLANT RESEARCH/AFOSR-ISSA-77-0001

Leon D. Strand and Norman S. Cohen

Jet Propulsion Laboratory, Pasadena, California

Nitramine propellants are of interest for gun and rocket propellant applications because they are an energetic source of smokeless combustion products. For the gun propellant application, there has been concern about the pressure exponent shift exhibited by these propellants at high pressure. However, differences in combustion behavior have been observed between closed vessel (transient pressure) and strand burning rate (constant pressure) experiments. Furthermore, there is evidence that the impact of the pressure exponent shift may be application-dependent. Analytical work based upon constant pressure (steady-state) modeling has suggested methods to avoid the exponent shifts. Nevertheless, transient pressure modeling is warranted because the application and the closed vessel experiments are in a transient pressure environment. It is desired to explain the differences between the steady-state and transient behavior in order to better evaluate the consequences of the exponent shift and improve the predictability of the ballistics. For the rocket propellant application, there has been concern about the combustion instability of smokeless propellants. Although considerable work has been done with ammonium perchlorate propellants, the effect of nitramines on combustion instability has not been systematically investigated. It is desired to acquire this information in order to provide a basis for future propellant tailoring.

Differences between closed vessel and strand burning rate data have been reviewed. It appears that nitramine propellants behave differently than homogeneous propellants, that homogeneous propellant behavior can be explained by simple P-dot theory but nitramine propellant behavior cannot. A theory is suggested based upon the surface structures of nitramine propellants observed and modeled in the prior steady-state work. It is proposed to incorporate these elements of the steady-state behavior into a time-dependent model. The timewise development of and changes in the surface structure will be coupled to a condensed phase time lag theory and the conservation equations for pressure. Model development is currently in progress. Propellants for the T-burner experiments have been selected and are being processed; results are not yet available.

COMBUSTION RESPONSE MODELING FOR COMPOSITE SOLID PROPELLANTS/ MIPR No. F04611-76-X-0050

N. S. Cohen, F. E.C. Culick, K. N. R. Ramohalli, L. D. Strand

Jet Propulsion Laboratory, California Institute of Technology
Pasadena, California

It is the aim of this research to obtain a theoretical understanding of combustion instability in rocket motors for use in the Air Force applications of missiles; specifically, it is the aim to account for, and suggest remedies for, combustion instability arising out of heterogeneity effects in the solid propellant.

The fundamental distinctive feature of this work is a model for ammonium perchlorate/inert binder low smoke (non-metallized) propellants that combines a "sideways sandwich" model* with exothermic decomposition in a surface melt layer. It is postulated that the active driving mechanism of combustion instability is the <u>condensed phase</u>. For the purposes of this analysis it is hypothesized that the condensed phase is adequately represented by alternate layers of crystalline ammonium perchlorate and the inert binder. The thickness of the AP crystal layer is equated to the AP particle size, and the thickness of the binder layers is computed from packing fractions (analogous to BDP treatments). It is also postulated that there exists at all times (in the pressure range of interest) a thin melt layer on the surface of the AP layer bordering the vapour phase. The melt layer is the site of exothermic decomposition of ammonium perchlorate. The vapour phase processes assume secondary importance, but are required to be modeled to the extent of supplying proper boundary conditions on the condensed phase. A simplified form of diffusion flame standoff distance is assumed.

Analytical solutions are obtained for the time-independent burning rate of the propellant in the limit of thin melt layers, which is a practical limit. The burning rates then lead to computations of the thermal wave penetration in the solid propellant. Typically, the penetration is observed to be of the order of magnitude of ten layers for realistic cases. However, artificial combination of a course size and high burn rate has shown a penetration of less than one layer. A decrease in size does not collapse the thermal wave proportionally. This has the implication that instability may be expected when the AP particle size is decreased to obtain high burn rate because the heterogeneity becomes important in relation to the thermal wave. Future work will derive pressure coupled response functions from solutions of the time-dependent burning rate model. Numerical solutions of the problem are envisioned. The time-independent component is being used to assist the formulation of the solution approach.

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* Similar to the work of Langellé, Law and Williams

T-BURNER VENT LOSSES

S. Murthy, J. Osborn and J. Renie

Purdue University
West Lafayette, IN

Abstract not submitted for publication.

DETERMINATION OF THE ADMITTANCES OF BURNING SOLID PROPELLANTS BY THE DRIVEN BURNER TUBE METHOD

B. T. Zinn, M. Salikuddin and B. R. Daniel

School of Aerospace Engineering
Georgia Institute of Technology
Atlanta, Georgia

On-going experimental and theoretical efforts which are concerned with the development of a new experimental technique for the measurement of the admittances of burning solid propellant samples are described. In this study a modification of the impedance tube technique is used to measure the burning propellant response over a wide range of frequencies. During the reporting period, improvements which included a more accurate method for computing the burner tube temperature distribution and a technique for determining the propellant response from pressure amplitude measurements only have been incorporate into the data reduction program. The Computation of the temperature distribution employs a nonlinear regression technique which provides the best fit between the theoretically predicted and the experimentally measured pressure wave pattern in the burner tube. This technique gives a temperature profile which is consistent with the measured wave structure. The use of amplitude data only in the determination of the propellant response factors has been introduced to eliminate the need to use measured phase data which is not sufficiently accurate when measured under low amplitude conditions.

A minicomputer-based data acquision system was incorporated into the data reduction scheme to obtain improved pressure data. This system processes the data in three stages. First, the analog signals from the transducer channels are sampled, digitized and stored at a controlled area. Next, the stored readings are processed by the computer. The measured data are digitally filtered and pressure amplitude and phase data are obtained at the frequency of interest for all of the test transducers. Finally, the pressure data are used in the data reduction scheme to obtain the needed admittance values.

Experimental efforts conducted at the high pressure facility have been concerned with the measurements of the admittances of a number of solid propellants at different frequencies. Data measured to date indicates that the tested propellants tend to amplify the burner tube oscillation at some instances and damp it at other. The causes of this unexpected behavior are currently under study. In contrast to the observed solid propellant behavior, good response factor data was measured in a related experiment in which the admittances of the gaseous injector elements were investigated using similar experimental and data reduction techniques.

HOLOGRAPHY OF SOLID PROPELLANT COMBUSTION
CONTRACT F04611-76-C-0053

R. F. Wuerker
R. A. Briones

TRW Defense and Space Systems Group
Redondo Beach, California

Application of the laser holographic technique opens a new dimension in the investigation of combustion of solid rocket propellants. It can provide increased capability in characterizing combustion phenomena. Through better understanding of combustion phenomena better analytical models can be developed to improve performance and combustion stability predictions for solid rocket motors. A three phase program is being conducted to demonstrate feasibility and develop the capability to apply the laser holography to quantitatively characterize 1) particle size, 2) particle velocity, 3) flame density gradients, 4) propellant surface characteristics and 5) particle spatial distribution. The purpose of each phase is: Phase I--Feasibility Demonstration, Phase II--Further Development and Verification and Phase III--Equipment Installation and Demonstration at the Air Force Rocket Propulsion Laboratory to provide the Air Force with an in-house capability to apply holography to solid rocket propellant combustion investigations.

Various holographic techniques are being investigated which include diffuse rear-illuminated, collimated, reflective, scattered light and holographic interferometry. The effects of parameters such as laser pulse width, beam intensity ratios and wavelength change between recording and reconstruction of the holograms are systematically being investigated.

The tests are being conducted using a pulsed ruby laser and a combustion window bomb operated at pressures of 500 and 1000 psig. Different solid propellant formulations are being tested. These include metallized (16-21% Aluminum) and nonmetallized (reduced smoke) propellants with burn rates ranging from .15-1.69 in./sec.

Results to date are very encouraging in that 3 micron resolution has been achieved in the pressurized combustion environment. Shortening the laser pulse width from 80 to 10 nanoseconds allows a clearer view of the region above the burning surface of high aluminum loaded propellants. Interferograms provide dramatic views of the thermal environment above the burning surface. The results achieved to date will be discussed in more detail during the presentation.

AUDIBLE AND ULTRASONIC EMISSIONS FROM COMPOSITE SOLID PROPELLANTS

AFOSR 75-2805

James I. Craig and Warren C. Strahle

School of Aerospace Engineering
Georgia Institute of Technology
Atlanta, Georgia 30332

This investigation deals with the measurement of the audible and ultrasonic acoustic emissions from burning solid propellants. By observing the characteristics of the audible frequency spectrum of the combustion noise, it is possible to relate the spectral features to specific combustion processes. Both the frequency spectrum and RMS amplitude are determined in the ultrasonic studies for correlation with propellant composition and burn rate uniformity.

A pressurized deflagration tube is used in this study and is instrumented with transducers which detect the audible and ultrasonic emissions from the deflagrating propellant. To date the effects of the following variables on the noise generated by the combustion process have been investigated:

(1) AP particle size
(2) aluminum addition
(3) aluminum coating (AFCAM)
(4) mean pressure (15 to 30 Atm)
(5) pressurization gas
(6) catalytic agent

Over 60 strands have been tested and each formulation has been tested more than once to verify the consistency of the data.

From the ultrasonic data the following observations have been made.

(1) Correlation between the RMS emission levels with burn rate indicate that the emission levels increase with the square of the burn rate. The data also show that, in tests where an abnormally high burn rate was observed, short periods of high emission levels, or "bursts," were also noted during the burn. The results indicate that the RMS signal level can be used as an indication the quality of the burn, and, perhaps, as a qualitative measure of the burn rate.

(2) For a given propellant composition, the spectral features of the ultrasonic emissions are unique. The spectral features change with time during the burn with an increase in higher frequency content with increasing time. In general, well-defined peaks occur at the 75-100 kHz range and at the 150-250 kHz range. Because the spectra are unique for a given propellant composition, the spectral characteristics may have use in assessing quality control in the production of solid propellants.

(3) By measuring the time from the onset to termination of the ultrasonic emissions, burn times can be measured accurately.

EVALUATION AND COMPILATION OF THE THERMODYNAMIC PROPERTIES OF HIGH TEMPERATURE SPECIES

Malcolm W. Chase

The Dow Chemical Company
Thermal Research
Midland, Michigan 48640

The JANAF Thermochemical Tables provide Air Force related activities with the best set of self-consistent thermodynamic data currently available in a well-established format which can be quickly and easily used. Our objective is to review the literature, evaluate the accuracy of the measurements, calculate thermodynamic functions, and publish thermochemical tables for use in the Air Force community.

There is a continual effort being made to add new chemical species to the tabulation as well as revise older (unreliable) species. The selection of species to be studied depends on current and future Air Force interests. In addition to these more obvious products of this project, there are other important studies in progress. The partition functions used in calculating gas phase thermochemical tables are being reanalyzed both in terms of extending the temperature range beyond 6000K and accounting for more precise molecular descriptions. Data treatment packages are in constant need of appraisal. Our 2nd and 3rd law treatment of equilibrium data is being reviewed in order to insure proper treatment of data and the relationship to other documented variations. Cooperative ventures are in progress to yield better internally consistent groups of tables through a simultaneous treatment of a wide variety of data. A series of review articles are also planned to better summarize the data (and lack thereof) in the alkaline earth, transition metal, and silicon area.

HYBRID FINITE ELEMENT MODELS FOR FRACTURE ANALYSIS

Satya N. Atluri*, K. Kathiresan**, and M. Nakagaki**

School of Engineering Science and Mechanics
Georgia Institute of Technology
Atlanta, Georgia

The work reported in this area is aimed at providing technology to enhance the Air Force's capability to assess the structural integrity of solid propellant rocket motors based on concepts of fracture mechanics. The technology being pursued is hybrid finite element analysis techniques for three dimensional crack problems, with or without material interfaces at the crack location.

This presentation briefly reviews the mathematical formulation of the hybrid finite element techniques and their application to analysis of cracks in homogeneous materials as well as at bi-material interfaces. The finite element method uses local approximate solutions to build up a solution for the entire domain. The hybrid finite element technique provides a straightforward way in matching the different types of local solutions for different regions. This feature is especially important for crack analysis, because it enables one to solve crack problems by properly matching the singular solutions near the crack front with the finite element solution for the rest of the domain. Since local approximate solutions of field equations are usually easy to construct (often in terms of polynomials) and the geometry is approximated as an assemblage of elements, the hybrid finite element technique makes it possible to analyze complicated crack problems in a routine manner. Therefore, it is an effective tool for stress analysis and prediction of fracture behavior.

In virtually all crack propagation situations in solid rocket motors, a bi-material interface such as the propellant-liner interface is eventually encountered. To study such situations, a "special bi-material hybrid crack element" is being developed to model cracks running along and/or in to bi-material interfaces. The presentation will include a summary of the progress made to date in the area of bi-material fracture analysis.

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* Associate Professor, ** Post-Doctoral Fellow

MATERIALS WITH VARIABLE BONDING

Michael H. Quinlan, NRC Resident Research Associate

Air Force Rocket Propulsion Laboratory
Edwards AFB, California

The Air Force has need of a valid constitutive theory for solid propellants in order to carry out rational design and structural analysis of rocket motors. The work reported in this paper provides the fundamental theoretical basis for valid propellant constitutive laws.

The effort conducted under this research associateship has dealt primarily with mathematical formulation of the theory from the most fundamental level through application to all classes of material behavior. Experimental propellant characterization is also being done to obtain numerical parameters for the propellant constitutive law.

This presentation briefly reviews the concepts involved in the recently completed theory on the bulk behavior of propellants. Insofar as the Cauchy stress labels a unique state of internal force at a point, the aforementioned theory provides a label for each state of bonding subjectively identified with the actual state of filler particle-to-polymer (binder) and polymer-to-polymer chemical bonding at a point. The crucial idea in effecting such a labeling is that of a stable sequence of deformations. These are sequences which do not alter the present state of bonding when the present deformation is held fixed for arbitrary amounts of time.

The task of experimentally exhibiting these sequences is fundamental in characterizing the constitutive law established by the theory. In addition to a discussion of this task, an overview of the entire program is presented.

LATTICE DYNAMICS IN HEATED HMX*

T. B. Brill and F. Goetz

Department of Chemistry
University of Delaware
Newark, Delaware 19711

This project is focused on detailing the fundamental events which occur in the cyclic nitramine, HMX, as it is heated to the degradation temperature. The heat sensitive vibrational motions are being studied in single crystals and powders using the light scattering technique of laser Raman spectroscopy.

It has been an accepted fact over the years that HMX exists in four different polymorphs called α, β, γ and δ-HMX. β-HMX is the material normally encountered at room temperature. However, α, γ and δ appear at higher temperatures and can be stabilized at room temperature under the right conditions. We have succeeded in recording for the first time the full vibrational spectrum of all of these materials. γ-HMX is said to be a "metastable" form and practically nothing is known about its structure. We have found that γ-HMX is very similar to the α and δ forms and is considered to be about halfway between the two in structural features. The most significant discovery to date has been evidence of a <u>fifth</u> polymorph into which β and α-HMX are found to pass above 140°C. We have been calling this polymorph γ'-HMX since it is like γ-HMX in many ways. It is routinely observed and definitely exists in our work. A new picture of the solid state behavior of heated HMX is thus emerging, and, although still preliminary, it will be presented. Also to be discussed are the results on polymorph interconversions which are not in all cases in accordance with the accepted patterns.

Some secondary caveats have emerged. The use of the hot-stage microscope to understand polymorph interconversions, while qualitatively useful, does not give the detail needed to understand the solid properties of HMX. Second, the heating rates and time spans at various temperatures greatly affect the results in a fundamental sense. Careful documentation of these parameters is needed.

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HMX THERMAL DECOMPOSITION

Mr. Berge B. Goshgarian

Air Force Rocket Propulsion Laboratory

Edwards AFB, CA 93523

Considerable R&D activity exists regarding the use of HMX as a replacement for AP in solid propellant formulations. Advantages include lack of primary and minimal secondary smoke, insensitivity from moisture attack, high specific impulse, and non-toxic as well as non-corrosive combustion products. Disadvantages include low burn rate, high pressure exponent, and poor physical properties. A basic understanding of HMX combustion chemistry is required so that appropriate combustion modifiers can be selected. The objective of this study is to develop ingredient selection criteria for tailoring ballistic properties of HMX propellants.

High pressure (2000 psi) differential scanning calorimetry (DSC) techniques will be used to obtain thermochemical information on HMX and HMX combustion modifier mixtures. A flow reactor coupled to a mass spectrometer will be used to obtain decomposition kinetic data on HMX and HMX combustion modifier mixtures.

Construction of the high pressure DSC cell is complete and preliminary tests have begun. Initial tests will include data acquisition on well characterized HMX samples to ascertain effects of pressure and heating rate on melting/decomposition temperatures, crystal transition, and other thermochemical parameters. These baseline runs will be followed by HMX-combustion modifier mixtures. The flow reactor-mass spectrometer system will be used to identify decomposition products from HMX as well as HMX-combustion modifier mixtures. Helium and/or helium plus mixtures of product gases will flow through a uniformally heated sample. Evolved gases will be mass spectrometrically analyzed. Kinetic rate data will be obtained and reaction mechanisms proposed.

The final phase of this study will include evaluation and verification of contractual and in-house HMX experimental data. Mechanisms for HMX decomposition and reactivity with combustion modifiers will be postulated. An ingredient selection criteria will be developed for modifying HMX propellant combustion characteristics in a desired manner for specific mission requirements.

SYNTHESIS OF NITROPOLYMERS

FREDERICK F. MYERS, JR., 1LT, USAF

AIR FORCE ROCKET PROPULSION LABORATORY/SOLID ROCKET DIVISION
EDWARDS AFB, CALIFORNIA

The Air Force has a technical need for binder systems containing energetic polymers to provide the minimum hazard, high performance minimum smoke propellants for tactical rocket motors. This basic research effort is designed to assess various energetic functional groups and their relationship to the desired propellant requirements. An overview of the requirements of the Air Force and the objectives in this area will be presented. The present technical effort is being directed at reactions involving allyl and glycidyl ethers with various nitro containing alcohols utilizing the reaction methods developed at Seiler Research Laboratories. Once the monomers have been synthesized, polymerization reactions will be attempted using standard methods.

SYNTHESIS OF BURN RATE MODIFYING ADDITIVES

Dr. Indu B. Mishra****

Air Force Rocket Propulsion Laboratory
Edwards AFB CA 93523

Some Air Force applications require burn rate enhancement catalysts. Both ferrocene derivatives as well as carboranes are known to be good catalysts for this purpose. Additive catalytic effect is expected when the two functionalities are combined as in metallocarboranes (π -carbollyl transition metal compounds). With this end in view, several metallocarboranes were synthesized and the effects of adding these as catalysts in solid propellant were investigated.

The compounds synthesized are:

1. $(CH_3)_4N \cdot Ni(III)(o\text{-}B_9C_2H_{10} \cdot n\text{-}C_6H_{13})_2$*
2. $Ni(IV)(o\text{-}B_9C_2H_{10} \cdot n\text{-}C_6H_{13})_2$
3. $(CH_3)_4N \cdot Fe(III)(o\text{-}B_9C_2H_{11})_2$
4. $(CH_3)_4N \cdot Cu(III)(o\text{-}B_9C_2H_{11})_2$
5. $[Cu(II)(NH_3)_4][Fe(III)(o\text{-}B_9C_2H_{11})_2]_2$
6. $[Cr(III)(en)_3][Fe(III)(o\text{-}B_9C_2H_{11})_2]_3$**
7. $[Fe(Cp)_2][o\text{-}B_9C_2H_{12}]$***

The catalytic effect of certain complex ferro- and ferri-cyanides will also be presented.

* o=ortho
** en=ethylene diamine
*** cp=cyclopentadienyl
**** National Research Council, Resident Research Fellow, 1976-77

METAL ION STABILIZERS

** N. S. Viswanathan and Robert C. Corley

AFRPL/MKPA, Edwards AFB CA 93523

The requirement for end burning missiles such as SRAM-X dictates a high burning rate without introducing a high pressure exponent. Copper compounds are generally the best solid catalysts for lowering the pressure exponent, but they create processing and aging problems. This program is designed to develop means for incorporating copper compounds into solid propellants without encountering the processing and aging problems. This investigation is divided into two parts: (1) studies on the effects of metal cations on cure reactions of composite propellants, (2) synthesis of metal salts/chelates as burn rate modifiers of composite propellants.

Several investigations have been aimed at the catalytic effects of transition metals, particularly iron, copper and chromium, on burn rates. The inherent disadvantage of these metals is that they cause spurious side reactions, such as crosslinking of the HTPB propellants by free radical processes.

In the present work, copper compounds have been examined in great detail for their potential use as burn rate additives. Following are the approaches taken for this study:

1. Synthesis of copper chelates with high stability and chelated to the highest coordination level.

2. Analagous to the studies of iron, "in situ" chelation of the active metal ions.

3. Examination of the effects of these ions on the cure kinetics by isocyanate estimations using the traditional amine reaction and HTPB-isocyanate reaction rates as internal standards.

4. Development of a model for the autoxidative polymerization and testing of its validity.

5. Measurement of induction times for oxidation for various compositions of the HTPB using a constant volume oxidation setup (Warburg type).

The current status of these experiments from 1 Oct 76 to date will be reviewed.

** NAS-NRC Senior Research Associate sponsored by AFSC.

STUDY OF THE CONSEQUENCES OF THE FLOW OF HIGH-PRESSURE, HIGH-TEMPERATURE GASES INTO PROPELLANT CRACKS

A. Takata and A. Wiedermann

IIT Research Institute
Chicago, Illinois

This study involves the development of a computerized model with which to identify the causes of solid propellant rocket motor detonations during firing. This model treats the problem of suddenly exposing one end of a propellant crack (or flaw or debond) to gases at higher pressures and temperatures than those associated with the gases initially in the crack. Simplified analyses are used to treat the problems of

- gas dynamics
- heating of crack surfaces
- burning
- mechanical deformations of cracks due to internal pressures and reflected stress waves

The downstream end of the cracks may be open or closed. Initial crack widths may vary with depth.

This paper elaborates on means used to predict crack heating and regression rates. Model results are presented showing the relative importance of various factors upon rapid pressure rises. This endeavor involved the hypothetical case of no mechanical deformations. Sensitivity studies involved the following:

- rates of convective heating
- rates of heat feedback from burning propellant (internal plus heat conduction across gas layer)
- chamber pressure
- crack widths

A highly important causal factor of pronounced, rapid pressure rises is the internal heating. If and when the regression rates commence to rise above the steady burning rate associated with the prevailing pressure, internal heating can lead to pronounced pressure rises subject to two conditions. These are provided the crack is sufficiently thin and long to deter the escape of gases and provided relatively large amounts of sensible heat have been stored in the propellant by prior heating. Effects of partial crack collapse due to reflected stress waves will act to accentuate the resultant pressure rises. This feature of the model is presently being revised to accomodate order of magnitude variations in the crack width caused by reflected stress waves.

MODELING THE DEFLAGRATION-TO-DETONATION TRANSITION IN REACTIVE SOLID PARTICLE-GAS MIXTURES*

Herman Krier (Principal Investigator)

University of Illinois at Urbana-Champaign
Urbana, IL 61801

The ability to predict a transition from a subsonic convectively-driven deflagration wave to a detonation in porous granular explosives or high energy granulated solid propellant requires an accurate ability to describe the reactive two-phase fluid mechanics of such systems. A major part of the effort is to develop criteria for the critical run-up length to detonation as a function of the granulated bed porosity, the chemical energy per unit mass of the solid material, and the propellant burning rate.

The modeling includes a study of the basic concepts for the rigorous formulation of a reactive system in two phases. Several models are being considered which differ in the derivation of the two-phase conservation equations based on the center of mass of each phase, and one based on the center of mass of the mixture. Concepts using continuum mechanics based on homogeneous phases occupying the same domain versus multi-phase mechanics based on a heterogeneous mixture of phases in the same space, but mutually exclusive are being tested.

The work underway also includes our preliminary efforts to account for particle-particle interaction, since in the highly transient flows leading to the extreme pressure wave buildup, the propellant granuals are compacted forward and must resist their own motion by particle-particle collision. Also to be included are discussions concerning the numerical integration schemes to solve the nonlinear set of coupled partial differential equations.

*AFOSR Grant 77-3115

DEFLAGRATION TO DETONATION TRANSITION IN HMX-BASED PROPELLANTS*

M. Cowperthwaite and J. T. Rosenberg
Stanford Research Institute

The long range objective of the research is to develop the capability of assessing the deflagration to detonation transition (DDT) hazard in HMX-based propellants. A combined experimental and theoretical program has been started to develop the basic understanding of DDT required to achieve this objective. Included in this program are specific tasks to elucidate mechanisms of DDT, to establish conditions for its occurrence, and to formulate a satisfactory model for its quantitative description. The newly developed Lagrange gage technology will be used to obtain the quantitative description of the flow in burning propellants required to make progress on all of these tasks.

Experiments are being designed to ascertain whether the existence of a crack field in burning HMX propellants is necessary for the onset of DDT, and to examine the dependence of DDT on the properties of such a crack field. Multiple Lagrange stress gages will be used to record stress histories produced ahead of the flame front in buring HMX propellants with and without a simulated crack field. The pressure histories will be used to determine the flow fields and the conditions for the onset of DDT.

Modeling studies are being undertaken in the first phase of the theoretical program to improve the existing treatment of DDT. These studies include the formulation of a more realistic treatment of the flow produced by a nonsteady flame and the establishment of conditions for its acceleration. In the second part of the theoretical program, the results of the experimental studies will be used to improve the model of DDT.

*Research sponsored under AFOSR Contract F49620-77-C-0039.

ANALYSIS OF THE COMBUSTION-TURBULENCE INTERACTION ON AN EROSIVELY-BURNING SOLID PROPELLANT

R. Beddini, A. Varma, and E. Fishburne

Aeronautical Research Associates of Princeton, Inc.
Princeton, New Jersey 08540

Burning rate augmentation due to erosive combustion must be accurately accounted for in considering overall solid propellant motor performance. Further, recent design trends to low port-to-throat area ratio motors accentuate this phenomenon. Contemporary theories of erosive burning are mainly correlations to data in the erosive burning regime and do not properly account for the physical aspects of propellant combustion with large convection.

In the present method, the problem of erosive burning is being approached through a detailed modeling and calculation of the reacting turbulent boundary layer on the propellant surface. Emphasis on the gas phase combustion-turbulence interaction is considered important and justified, as this area is phenomenologically not well understood. Solid phase coupling has been achieved initially for the simpler (homogeneous) propellant types. The implementation of boundary conditions appropriate for composite propellants is intended for a later stage of research.

During the past year, results have been reported (JANNAF Combustion Meeting, September 1976) using the A.R.A.P. Solid Propellant Erosive Combustion (ASPEC) technique, coupled with a modeled homogeneous propellant. These results display some of the essential features of erosive burning such as threshold velocity, nonlinear burn rate velocity response, and the transient burn rate response near the start of a propellant sample. An important result is that erosive burning appears coincident with turbulence entering the combustion zone. Furthermore, only basic propellant thermodynamic and strand burn rate data are required for these studies. Work is proceeding with the immediate objective of removing some restrictions from the present method.

THEORETICAL AND EXPERIMENTAL INVESTIGATION OF EROSIVE BURNING OF NON-METALLIZED COMPOSITE SOLID PROPELLANTS

K Kuo, M Razdan and R Kovalcin

The Pennsylvania State University
University Park, PA 16802

The overall objective of the current research is to achieve a basic understanding of the erosive burning mechanism in solid-propellant rocket motors. Both theoretical and experimental studies are undertaken. In the theoretical modeling, a reactive turbulent boundary-layer approach is used to analyze the erosive burning phenomenon. A second-order turbulence closure has been selected in the theoretical formulation. The theoretical model can be used to study the effect of gas velocity, pressure, stream-wise pressure gradient, oxidizer particle size, and oxidizer-to-fuel ratio. For model validation, a test rig has been designed to establish a two-dimensional, turbulent boundary layer flow over a flat plate. The test rig can operate under various gas-dynamic conditions. A Laser-photodiode servomechanism has been developed to measure the burning rate, and preliminary tests have demonstrated successful operation of the apparatus.

STUDY OF EROSIVE BURNING PHENOMENA IN COMPOSITE PROPELLANTS

Merrill K. King

Atlantic Research Corporation, Alexandria, Virginia

Increasing development of low port-to-throat area ratio solid rocket motors and nozzleless rocket motors, with resultant high velocity crossflow of combustion products across burning propellant surfaces, is leading to increased occurrence and severity of burning rate augmentation due to these crossflows (erosive burning). Development of a better understanding of the effects of such crossflows on solid propellant combustion is needed for accomplishment of accurate motor performance. With such understanding, the motor designer can either design his grains to compensate for mean erosive burning effects on grain burn pattern, or, knowing how propellant formulation parameters affect erosion sensitivity, vary propellant parameters in such a way as to minimize these effects. Due to the expense and complexity of erosive burning testing, it is highly desirable that a realistic predictive model, requiring at most strand burning rate data (no crossflow) as data input and yielding predicted dependence of burning rate on pressure and crossflow velocity, be developed. Such a model would be useful both to the motor designer in performing interior ballistics design analysis and to the formulator in predicting the effects of formulation changes on propellant erosion sensitivity.

Past modeling efforts in the area of erosive burning of solid propellants have been reviewed and lack of a model which incorporates a realistic description of composite propellant combustion has been noted. A possible physical mechanism by which crossflows may affect the combustion of a composite propellant through bending of diffusion flames has been postulated and a mathemetical model for prediciton of the burning rate of a composite propellant in such a crossflow, given only the no-crossflow burning rate versus pressure characteristics of the propellant, has been developed. This model has been used to predict remarkably well the erosive burning characteristics of a propellant studied by Saderholm. A second generation model which will not require no-crossflow data, but will permit prediction of burning rate as a function of pressure and crossflow velocity, given only the propellant composition and ingredient sizes is currently being developed. This model contains some elements of the Beckstead-Derr-Price model (but with considerable modification) for no-cross flow composite propellant combustion, coupled with the flow analysis used in the first generation model and the same picture of bending of the diffusion flames.

In addition, a test device for studying erosive burning characteristics of a propellant in high velocity crossflow (up to Mach 1) has been designed and constructed and testing begun. To date, one formulation has been fairly extensively characterized regarding its burning rate-pressure-crossflow velocity relationships. Comparison of experimental results with predictions made using the first generation model mentioned above is encouraging. A series of motors and test grains of three additional formulations involving systematic variations from the first formulation have been designed and prepared, and will be tested shortly.

BEHAVIOR OF ALUMINUM IN COMBUSTION OF SOLID ROCKET PROPELLANTS

E. Price and R. Sigman

The Georgia Institute of Technology
Atlanta, GA

Abstract not submitted for publication.

HYDRAZINE DECOMPOSITION FOR MONOPROPELLANT PROPULSION SYSTEMS

A. C. Baldwin, D. M. Golden, K. Lewis, R. T. Rewick, and H. Wise

Stanford Research Institute, Menlo Park, California 94025

This research has for its objective identification and modification of the surface reactions responsible for gradual deactivation of alumina-supported iridium catalyst (Shell-405) employed in hydrazine monopropellant thruster. Earlier work had demonstrated that intermediate products of the hydrazine decomposition reaction cause chemical deactivation. Such build-up of surface intermediates gradually reduces the specific activity of the catalyst for hydrazine decomposition and contributes to performance decline of the monopropellant thruster.

In an attempt to elucidate the mechanism of catalyst deactivation encountered during pulse-mode operation of hydrazine fuel thrusters, we have investigated the kinetics of the reaction between hydrazine and Shell-405 catalyst at low pressures ($< 10^{-3}$ torr) in a Knudsen cell flow reactor. Two distinct temperature regimes have been observed. Above 600 K the reaction $N_2H_4 \rightarrow NH_3 + \frac{1}{2} H_2$ occurs at a rate independent of the previous hydrazine exposure to hydrazine, below 550 K the reaction $3N_2H_4 \rightarrow 4NH_3 + N_2$ takes place at a rate which depends on the previous treatment of the catalyst. In this temperature range prolonged exposure of the catalyst to hydrazine produces a decrease in the rate of decomposition which is reversible by exposure of the catalyst to hydrogen at high temperatures ($\sim$ 1000 K). Detailed investigation of the kinetics and mechanism of the hydrazine decomposition reaction at 472 and 560 K shows a 3/4 order dependence over a 30-fold concentration range. Also, deactivation by background gases at $\sim 10^{-7}$ torr is readily apparent and this deactivation process appears to have a negative temperature dependence.

Studies by infrared absorption spectroscopy have identified the NH_2-surface intermediate as the precursor to catalyst poisoning. If the conditions favor hydrogen abstraction from the NH_2-adspecies rather than hydrogen addition and ammonia formation ($NH_2(s) + H \rightarrow NH_3$), the formation of strongly bound nitrogen adatoms occurs which results in nitriding of the surface Ir atoms.

To modify the debilitating effect of the nitrogen adspecies we have begun to examine the feasibility of catalyst modification. Two approaches are currently under study: (1) the synthesis of Ir-cluster catalysts in which the Ir metal dispersion is much higher than currently available, and (2) the preparation of bimetallic Ir catalysts in which the binding of nitrogen-containing adspecies is reduced by changing the surface and/or electronic properties of the solid.

HYDRAZINE ELECTROCHEMICAL STUDIES

Mr Herman H. Martens

AF Rocket Propulsion Lab. (DYC)

Propellants for Air Force extended mission satellites require precisely defined storability criteria. To this end, two problem areas can be identified. One is to explain and correlate existing controversial corrosion data for metals in contact with monopropellant N_2H_4. Secondly, engineers have an imprecise predictive capability for performance of materials with N_2H_4. Information acquired will provide a means to define required propellant quality from the point of procurement through its duty cycle.

The approach will be to define the pertinant basic anhydrous hydrazine chemistry through application of currently available measurement devices.

The program is divided into three phases over a two year period: (a) to accurately measure the dissociation (autoionization) constant of anhydrous N_2H_4, (b) to determine the acidity or basicity of selected compounds (gases, liquids, solids) when dissolved in N_2H_4, and (c) to measure the half cell potentials of selected elements and some of their salts in N_2H_4.

Results to date of the first phase of the effort are presented.

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